



# Catalytic ozonation of chlorinated VOCs on ZSM-5 zeolites and alumina: Formation of chlorides

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## ABSTRACT

This study aims to understand the mechanisms and kinetics of chlorinated volatile organic chemicals (VOCs) removal during the catalytic ozonation process on  $\gamma$ -alumina and ZSM-5 zeolites. Both the H-ZSM-5 and Na-ZSM-5 types with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios and counter ions ( $\text{Z1000H}:\text{SiO}_2/\text{Al}_2\text{O}_3 = 1000$ ,  $\text{Z900Na}:\text{SiO}_2/\text{Al}_2\text{O}_3 = 900$ ,  $\text{Z25H}:\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$  and  $\text{Z25Na}:\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ ) were studied. In order to fully understand the mechanisms behind the catalytic processes, degradation of VOCs and chlorides formation were investigated during both ozonation alone and catalytic ozonation on alumina and zeolites. The effects of pH and hydroxyl radical scavengers on the efficiency of catalytic ozonation on alumina and zeolites were also studied. The results revealed that, as opposed to alumina, zeolites promoted decomposition of VOCs. Furthermore, the decomposition of chlorinated VOCs resulted in the generation of chlorides at significantly higher levels when compared with ozonation alone. The presence of hydroxyl radical scavengers had no significant effect on the removal rates of VOCs and the generation of chlorides in the presence of zeolites. It is therefore suggested that catalytic ozonation of organic VOCs on zeolites proceeds via a non-radical mechanism that involves reactions of molecular ozone with pollutants adsorbed on the surface of zeolites.

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## 1. Introduction

Ozonation is of considerable importance in water treatment due to its disinfection ability and the high oxidation potential of ozone. However, from an economic point of view, and due to higher removal efficiencies, heterogeneous catalytic ozonation is preferred over single ozonation [1]. Therefore, heterogeneous catalytic ozonation systems have been studied in recent years to improve the efficiency of ozonation. Degradation of many organic compounds has been studied by employing various heterogeneous catalytic systems such as ozonation in the presence of activated carbons [2,3],  $\text{Al}_2\text{O}_3/\text{O}_3$  [4], zeolites/ $\text{O}_3$  [5,6] and  $\text{TiO}_2/\text{O}_3$  [7,8]. However, there are many controversies regarding the understanding of the mechanisms of these processes [9,10]. For example, some reports suggested that adsorption plays an important role in catalytic ozonation process [6,11,12] while others suggested that the adsorption may have negative effect on catalytic ozonation process [13]. The role of the catalyst is also unclear. According to some find-

ings catalysts decompose aqueous ozone leading to the production of hydroxyl radicals [11,14,15]. While other reports suggested that catalysts act as adsorbents for both ozone and pollutants to facilitate surface reactions [6,12,16]. In addition to above, it is important to mention here that the same catalyst has been reported to be effective for some pollutants [17,18] and in some other reports it was found to be ineffective for other types of pollutants [17,19,20]. Therefore, it is indeed important to better understand the process of catalytic ozonation in order to scale-up this technology from lab to an industrial scale.

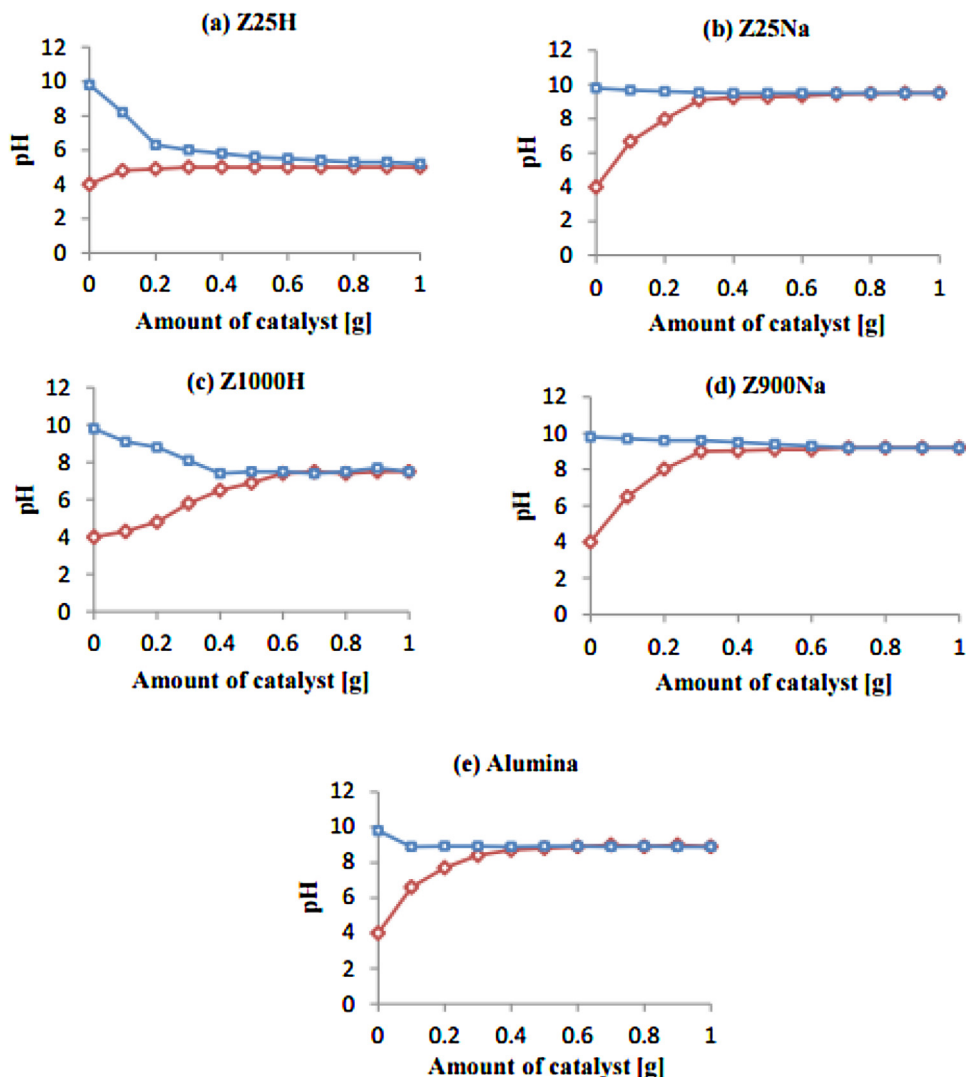
Different types of pollutants have been used to study the catalytic ozonation process in the presence of zeolites and alumina. There are however several, often contradictory, views on the catalytic activity of both catalysts. Some reports suggested that these catalysts do not decompose aqueous ozone [5,6,21]. However, others have hypothesised that both zeolites and alumina catalyse the decomposition of ozone leading to the production of hydroxyl radicals [15,17,22–25]. It is important to mention here that a lack of ozone decomposition does not indicate a lack of catalytic activity [16]. Some reports have suggested that Lewis and Bronsted acid sites of zeolites play a vital role in ozone decomposition leading to the production of hydroxyl radicals [15,25]. However, according to

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**Table 1**  
Physical properties of alumina and zeolites [3].

Material	SiO <sub>2</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mol ratio	Surface area (m <sup>2</sup> /g)	Average pore size (Å)	Point of zero charge
γ -alumina	0	100	–	190	47.8	8.9 ± 0.1
Z25H	90	5.4	30 ± 5	300	5.3	5.0 ± 0.2
Z1000H	99	0.1	1000 ± 5	300	5.3	7.5 ± 0.2
Z900Na	98	5.4	900 ± 5	300	5.3	9.2 ± 0.1
Z25Na	90	0.2	30 ± 5	300	5.3	9.5 ± 0.1



**Fig. 1.** Point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of ZSM-5 zeolites and alumina (Catalyst = 0.1–1.0 g;  $T = 25^\circ\text{C}$ ; electrolyte  $\text{NaCl} = 10^{-3} \text{ mol/dm}^3$ ;  $V = 190 \text{ mL}$ ).

some recent findings, ZSM-5 zeolites do catalyse the degradation of pollutants by molecular ozone reactions with pollutants [4,6]. Furthermore, it has been suggested that adsorption of pollutants plays an important role in the catalytic ozonation process [9,13]. Studies of the catalytic activity of alumina indicate that alumina does show catalytic activity for the degradation of certain pollutants [13,17,26], while it does not catalyse the removal of other pollutants such as hydrocarbons [17,19,27]. Recently, Nawrocki et al. [11] suggested that alkaline impurities present in alumina oxides may be responsible for ozone decomposition and hydroxyl radicals generation [10]. Therefore, it is important to monitor pH during the catalytic ozonation process.

This paper aims to provide further understanding of the mechanisms of ozonation of volatile organic chemicals (VOCs) such as cumene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene on zeo-

lites and alumina. For this purpose a comparative study has been conducted to verify the removal of cumene and chlorobenzenes from water. Chlorinated aromatic compounds are highly toxic, widely used and are known to be highly resistant to ozonation as compared to non-chlorinated compounds (benzene) [29]. This may be due to the steric effects of attached chlorinated groups. This paper is a continuation of our previous studies which concerned the removal of VOCs in the presence of zeolites [6] and alumina [17]. It has been hypothesised that zeolites catalysed the removal of VOCs by direct ozone attack on the surface of zeolites [6]. Alumina was found to be ineffective in the degradation of VOCs [17]. The present study focusses on new important aspects of catalytic ozonation, which are key to fully understanding the catalytic process. These include mechanistic studies of VOCs decomposition and chloride ions ( $\text{Cl}^-$ ) formation during the catalytic ozonation process in the

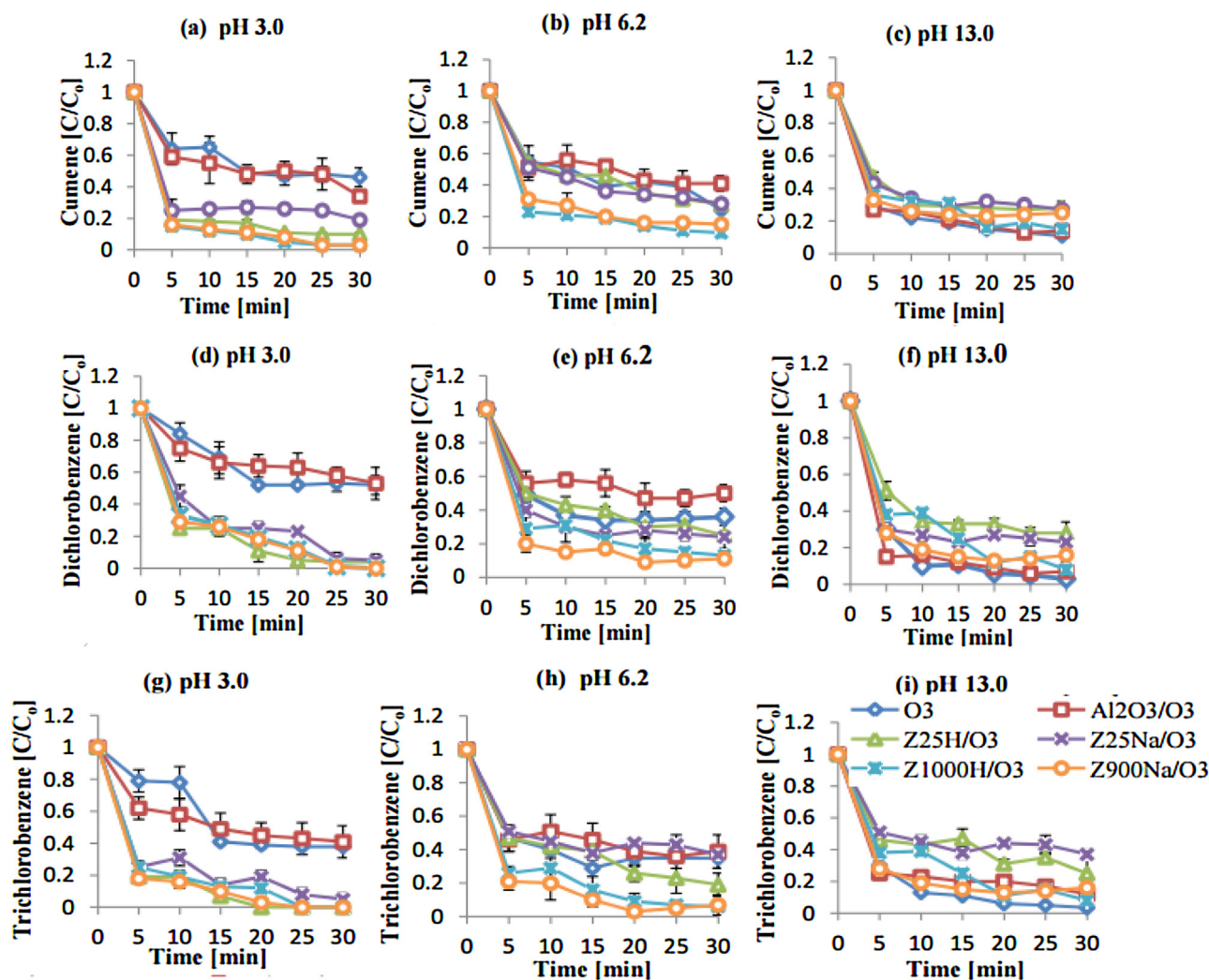


Fig. 2. Effect of pH on VOCs removal by ozonation alone and ozonation in the presence of ZSM-5 zeolites and alumina ( $C_0$  (cum) =  $19.2 \pm 0.5$  mg/L,  $C_0$  (DCB) =  $3.5 \pm 0.2$  mg/L, and  $C_0$  (TCB) =  $0.5 \pm 0.1$  mg/L;  $T = 20^\circ\text{C}$ ; pH = 3.0, 6.2 and 13.0;  $pH_{30\text{min}} = pH_0 \pm 0.3$ ; catalyst amount = 5 g;  $V = 490$  mL;  $O_3 = 0.1$  mg/min) [5,11].

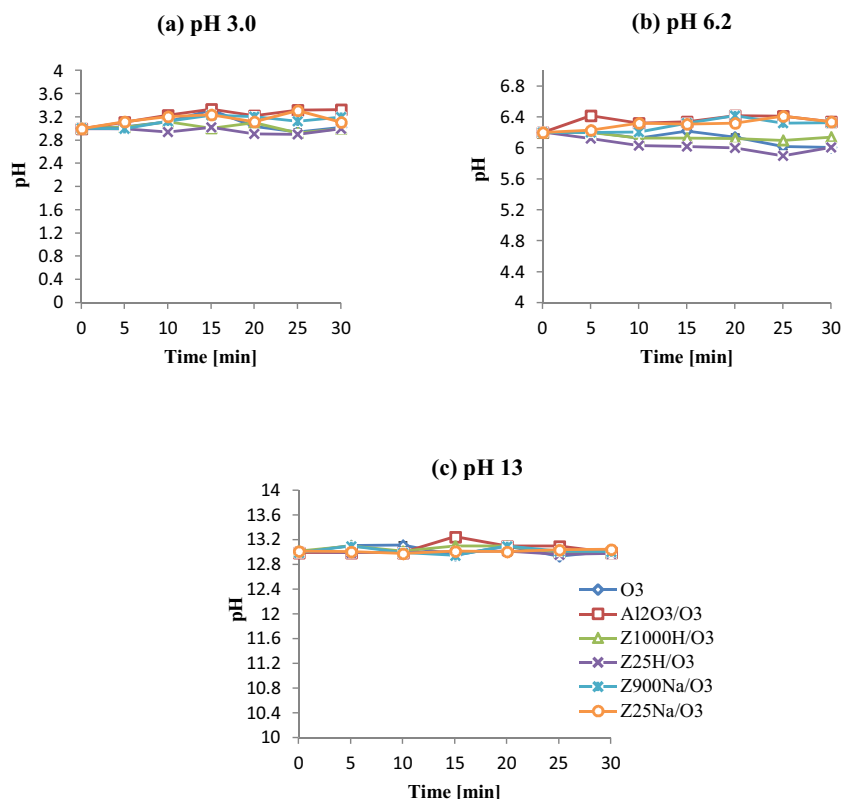
Tables 2

First order decomposition rates of cumene, dichlorobenzene and trichlorobenzene in  $O_3$ , zeolites and  $Al_2O_3/O_3$  processes.

Process	$K_{\text{overall}} \times (10^{-2} \text{ min}^{-1})$								
	pH = 3.0			pH = 6.2			pH = 13.0		
	Cumene	Dichlorobenzene	Trichlorobenzene	Cumene	Dichlorobenzene	Trichlorobenzene	Cumene	Dichlorobenzene	Trichlorobenzene
$O_3$	$2.65 \pm 0.2$ ( $R^2 = 0.912$ )	$1.95 \pm 0.3$ ( $R^2 = 0.953$ )	$3.06 \pm 0.3$ ( $R^2 = 0.805$ )	$3.03 \pm 0.2$ ( $R^2 = 0.933$ )	$3.06 \pm 0.2$ ( $R^2 = 0.802$ )	$3.28 \pm 0.2$ ( $R^2 = 0.897$ )	$3.92 \pm 0.3$ ( $R^2 = 0.910$ )	$5.86 \pm 0.3$ ( $R^2 = 0.909$ )	$4.87 \pm 0.3$ ( $R^2 = 0.812$ )
$Al_2O_3/O_3$	$2.75 \pm 0.2$ ( $R^2 = 0.901$ )	$1.60 \pm 0.2$ ( $R^2 = 0.939$ )	$2.68 \pm 0.2$ ( $R^2 = 0.950$ )	$3.00 \pm 0.3$ ( $R^2 = 0.916$ )	$1.95 \pm 0.3$ ( $R^2 = 0.906$ )	$2.89 \pm 0.3$ ( $R^2 = 0.820$ )	$4.12 \pm 0.3$ ( $R^2 = 0.862$ )	$5.27 \pm 0.2$ ( $R^2 = 0.901$ )	$5.18 \pm 0.3$ ( $R^2 = 0.848$ )
Z25H/ $O_3$	$7.35 \pm 0.3$ ( $R^2 = 0.911$ )	$6.33 \pm 0.3$ ( $R^2 = 0.743$ )	$4.05 \pm 0.2$ ( $R^2 = 0.875$ )	$3.46 \pm 0.2$ ( $R^2 = 0.867$ )	$3.89 \pm 0.2$ ( $R^2 = 0.917$ )	$4.05 \pm 0.2$ ( $R^2 = 0.904$ )	$3.71 \pm 0.2$ ( $R^2 = 0.876$ )	$3.73 \pm 0.3$ ( $R^2 = 0.832$ )	$3.56 \pm 0.3$ ( $R^2 = 0.847$ )
Z1000H/ $O_3$	$9.55 \pm 0.3$ ( $R^2 = 0.930$ )	$8.17 \pm 0.4$ ( $R^2 = 0.915$ )	$8.21 \pm 0.3$ ( $R^2 = 0.884$ )	$6.85 \pm 0.3$ ( $R^2 = 0.8904$ )	$5.92 \pm 0.3$ ( $R^2 = 0.840$ )	$6.35 \pm 0.2$ ( $R^2 = 0.879$ )	$4.66 \pm 0.3$ ( $R^2 = 0.873$ )	$6.14 \pm 0.3$ ( $R^2 = 0.903$ )	$4.03 \pm 0.2$ ( $R^2 = 0.885$ )
Z25Na/ $O_3$	$5.62 \pm 0.3$ ( $R^2 = 0.980$ )	$6.87 \pm 0.4$ ( $R^2 = 0.932$ )	$3.09 \pm 0.3$ ( $R^2 = 0.883$ )	$3.75 \pm 0.2$ ( $R^2 = 0.901$ )	$3.76 \pm 0.4$ ( $R^2 = 0.806$ )	$3.09 \pm 0.2$ ( $R^2 = 0.948$ )	$4.34 \pm 0.4$ ( $R^2 = 0.887$ )	$4.37 \pm 0.4$ ( $R^2 = 0.868$ )	$2.6 \pm 0.3$ ( $R^2 = 0.757$ )
Z900Na/ $O_3$	$9.72 \pm 0.4$ ( $R^2 = 0.928$ )	$8.35 \pm 0.4$ ( $R^2 = 0.949$ )	$7.92 \pm 0.3$ ( $R^2 = 0.875$ )	$5.97 \pm 0.3$ ( $R^2 = 0.883$ )	$6.41 \pm 0.3$ ( $R^2 = 0.905$ )	$6.81 \pm 0.3$ ( $R^2 = 0.908$ )	$4.40 \pm 0.3$ ( $R^2 = 0.870$ )	$5.69 \pm 0.5$ ( $R^2 = 0.776$ )	$4.66 \pm 0.2$ ( $R^2 = 0.912$ )

presence of zeolites and alumina. The monitoring of the generation of chloride ions in ozonation and catalytic ozonation processes may further help to study the actual degradation of chlorinated organic compounds during the catalytic process [30]. Additionally, VOCs decomposition rates and chlorides generation have been studied in

the presence of TBA, a hydroxyl radical scavenger to further understand the catalytic process. Furthermore, the rate equations have been calculated to investigate the order of reactions. In order to verify the catalytic processes occurring on alumina and zeolites, the effect of initial pH and the effect of hydroxyl radical scavengers



**Fig. 3.** pH changes during the removal of VOCs by ozonation alone and ozonation in the presence of ZSM-5 zeolites and alumina (Co (cum) =  $19.2 \pm 0.5$  mg/L, Co (DCB) =  $3.5 \pm 0.2$  mg/L, and Co (TCB) =  $0.5 \pm 0.1$  mg/L;  $T = 20^\circ\text{C}$ ; pH = 3.0, 6.2 and 13.0;  $\text{pH}_{30\text{min}} = \text{pH}_0 \pm 0.3$ ; catalyst amount = 5 g;  $V = 490$  mL;  $\text{O}_3 = 0.1$  mg/min).

on the removal of VOCs and generation of chloride ions have also been investigated.

## 2. Experimental

### 2.1. Materials and reagents

The ZSM-5 zeolites were supplied by Zeochem Switzerland and  $\gamma$ -alumina was supplied by Alcoa Inc, USA. VOCs were obtained from Sigma-Aldrich. All chemicals were of analytical grade and were used without further purification.

### 2.2. Ozonation experiments

Ozonation experiments were performed in a semi-continuous mode at room temperature ( $20^\circ\text{C}$ ) (column length, 70 cm; width, 51 mm; catalyst bed height, 5 cm) [6]. Possible loss of VOCs due to volatilization was also determined. A saturated solution (490 mL) of VOCs was used in the ozonation experiments and was prepared by directly spiking of VOCs to a flask containing 1 L of ultrapure water [6]. VOCs solution (cumene,  $19.1 \pm 0.5$  mg/L; 1,2-dichlorobenzene,  $3.5 \pm 0.3$  mg/L; 1,2,4-trichlorobenzene,  $0.5 \pm 0.1$  mg/L) was transferred to the column containing 5.0 g of catalyst, and was recirculated at a flow rate of 15 mL/min over the period of 30 min. Ozone was produced by a corona discharge method from pure oxygen by AZCO HTU-5000GE-120 ozone generator. By the aid of a ceramic sparger, ozone was continuously bubbled through the column at a flow rate of 0.1 mL/min. Samples were collected at 5 min intervals and quenched with 0.025 M  $\text{Na}_2\text{SO}_3$  in order to remove residual ozone. All the samples were filtered (PTFE 0.45  $\mu\text{m}$  syringe filter) prior to the analysis.

### 2.3. Analytical procedures

#### 2.3.1. Ozone dose

Gas phase ozone concentrations were determined by the iodometric method [31]. For this purpose the gaseous ozone was bubbled through a ceramic sparger into two sets of glass bottles, each filled with 200 mL of 2% KI [31]. Solutions were acidified with 10 mL of 1N HCl and the liberated iodine was titrated with standard 0.005 N  $\text{Na}_2\text{S}_2\text{O}_3$  using a starch indicator.

#### 2.3.2. Analysis of VOCs

VOCs were quantified by gas chromatography coupled with mass spectrophotometry (GC/MS, Agilent) as described previously [6]. The method was validated. The RSD was found to be less than 5%.

#### 2.3.3. Analysis of chloride ions

Chlorides concentrations were determined by ion chromatography using a DIONEX DX-120 system with Ion Pac As14 analytical column ( $4 \times 250$  mm) and Ion Pac AG14 guard column ( $4 \times 250$  mm) coupled to an ED-50A electrochemical detector (Dionex, USA). The limits of detection and quantification for phosphates were 0.05 ppm and 0.2 ppm respectively. The RSD was less than 5%.

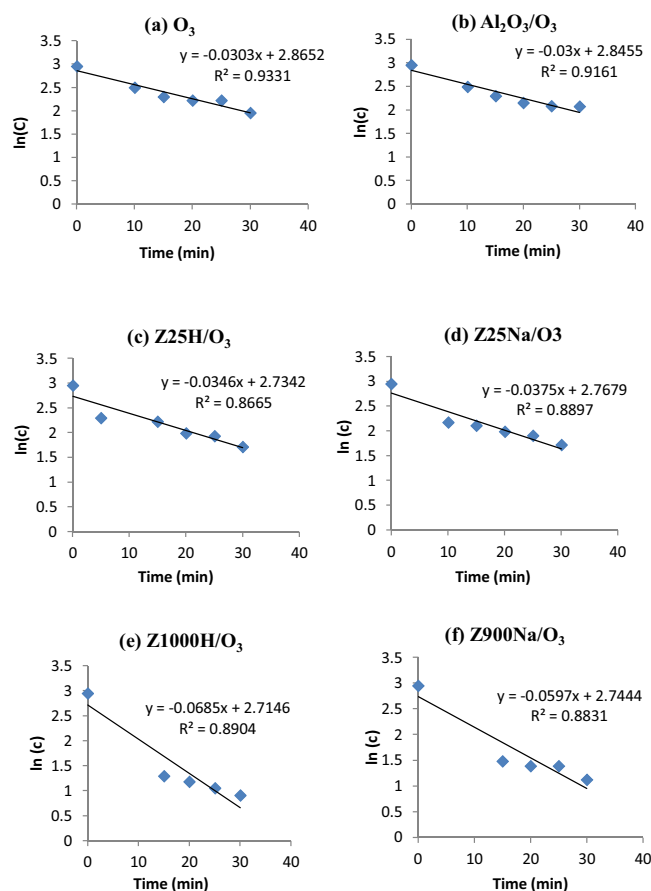
## 3. Results and discussion

### 3.1. Physicochemical properties of zeolites and alumina

Data regarding physical properties of zeolites were obtained from Zeochem Switzerland (Table 1). The point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of zeolites and alumina were determined using potentiometric mass titration method [32]. The point of zero charge of alumina was found to be 8.9 while the point of zero charge of zeo-

**Tables 3**Effect of TBA on the first order decomposition rates of cumene, dichlorobenzene and trichlorobenzene in O<sub>3</sub>, zeolites and Al<sub>2</sub>O<sub>3</sub>/O<sub>3</sub> processes.

Process	$K_{\text{overall}} \times (10^{-2} \text{ min}^{-1})$								
	pH = 3.0			pH = 6.2			pH = 13.0		
	Cumene	Dichlorobenzene	Trichloro benzene	Cumene	Dichlorobenzene	Trichloro benzene	Cumene	Dichlorobenzene	Trichloro benzene
O <sub>3</sub> (TBA)	3.24 ± 0.3	1.75 ± 0.3	2.95 ± 0.2	2.02 ± 0.1	2.45 ± 0.2	2.95 ± 0.2	2.95 ± 0.2	4.91 ± 0.2	4.01 ± 0.3
Al <sub>2</sub> O <sub>3</sub> /O <sub>3</sub> (TBA)	3.01 ± 0.3	1.68 ± 0.2	2.54 ± 0.2	2.03 ± 0.2	1.81 ± 0.3	2.61 ± 0.2	3.12 ± 0.2	4.65 ± 0.2	3.85 ± 0.2
Z1000H/O <sub>3</sub> (TBA)	9.31 ± 0.4	7.13 ± 0.4	8.35 ± 0.3	6.65 ± 0.2	5.56 ± 0.3	6.01 ± 0.3	3.92 ± 0.4	5.65 ± 0.3	3.65 ± 0.3

**Fig. 4.** First order plots for the removal of cumene in ozonation alone and ozonation in the presence of ZSM-5 zeolites and alumina ( $C_0$  (cum) =  $19.2 \pm 0.5$  mg/L;  $T = 20^\circ\text{C}$ ; pH = 6.2; catalyst amount = 5 g;  $V = 490$  mL;  $O_3 = 0.1$  mg/min).

lites ranged from 5 to 9.5 (Fig. 1). The average pore size was found to be 47.8 Å and the surface area of alumina used was 190 m<sup>2</sup>/g.

### 3.2. Catalytic ozonation of VOCs

#### 3.2.1. Kinetic study

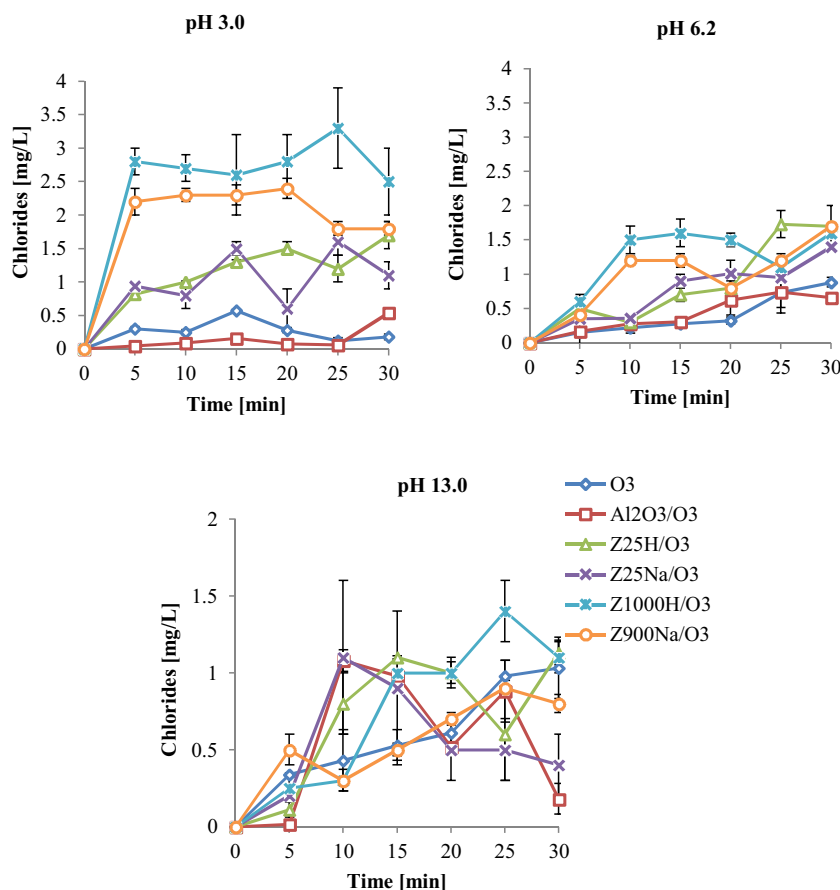
Catalytic ozonation of VOCs on alumina and ZSM-5 zeolites with different silica to alumina ratios were studied at selected pH values: 3.0, 6.2 and 13.0. The results presented in Fig. 2 show that alumina does not have catalytic activity for VOCs, while ZSM-5 zeolites show significant catalytic activity especially at pH 3 (Fig. 2).

Kinetic studies of catalytic ozonation for the removal of cumene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene were undertaken (Table 2). The catalytic process was found to follow the first order kinetics as indicated by the linear regression values in Fig. 4. Therefore, first order rate constants for the removal of VOCs have been determined (Table 2). The results clearly indicate that VOCs decomposition rates are higher in the case of catalytic ozonation in the presence of zeolites (Table 2) when compared with single ozona-

tion and ozonation in the presence of alumina (at pH 3 and 6.2). For example, first order decomposition rate constant for dichlorobenzene was calculated to be 15 times higher in the case of ozonation on zeolites when compared with ozonation alone (Table 2). The results further show that the rate constant values for ozonation in the presence of zeolites were found to be the highest at pH 3 when compared with pH 6.2 and 13 (Table 2). This may be due to the stability of molecular ozone at low pH which results in its higher adsorption on the zeolites surface, and which subsequently leads to faster decomposition of adsorbed pollutants [6]. It is worth noting that zeolites having higher silica to alumina ratios (Z1000H, Z900Na) are found to be more effective when compared with those with lower silica to alumina ratio (Z25H, Z25Na). This phenomenon can be explained by higher hydrophobicity of high silica zeolites leading to higher sorption of VOCs on their surfaces [12]. The results further show that higher decomposition rates on zeolites at pH 3.0 were observed for cumene when compared with chlorobenzenes. For example, the rate constant for VOCs degradation on Z1000H/O<sub>3</sub> at pH 3.0 was  $9.55 \times 10^{-2} \text{ min}^{-1}$ ,  $8.17 \times 10^{-2} \text{ min}^{-1}$ ,  $8.21 \times 10^{-2} \text{ min}^{-1}$  for cumene, dichlorobenzene and trichlorobenzene respectively (Table 2). This may be due to higher adsorption of cumene on studied zeolite when compared with chlorobenzenes [6]. Other explanation could be that chlorinated VOCs may be more resistant to ozone attack due to steric effects.

Previous kinetic studies [17] on heterogeneous process in the presence of alumina indicated that surface reactions are important in the catalytic process. Therefore, it is hypothesised that adsorption on the surface of the catalyst is vital in the catalytic ozonation process [17]. Furthermore, we postulate that molecular ozone reactions are fundamental to achieving effective VOCs oxidation with ozone while using zeolites as catalysts. It is important to mention here that ozone decay rates in the absence of pollutants were investigated by our group in previous studies [4]. The results indicated that alumina possesses high aqueous ozone decomposition rates when compared with zeolites. However, interestingly, in this work alumina did not show any significant catalytic activity for VOCs removal. This may be due to the lack of adsorption of VOCs on alumina. In our previous work, we reported that adsorption of studied VOCs on alumina [17], as opposed to ZSM-5 zeolites [6], is limited. Furthermore, as already mentioned, zeolites with high silica to alumina ratios have higher adsorption capacity towards VOCs. This is in correlation with our results which indicates that high silica zeolites (Z1000H, Z900Na) show higher catalytic activity as compared with low silica zeolites (Z25H, Z25Na). Qi et al. [11] has recently studied the catalytic ozonation of phenacetin on manganese ferrite and nickel ferrite. It was observed that adsorption of a pollutant and its intermediates play an important role in catalytic ozonation process. It was suggested that possible desorption of the pollutant and its intermediates from the surface of manganese ferrite may be one of the reasons for its lower catalytic activity as compared with nickel ferrite. This further supports our hypothesis that adsorption plays a key role in the catalytic ozonation process. The other explanation could be that molecular ozone reactions are favoured in the





**Fig. 5.** Effect of pH on chlorides formation during VOCs ozonation alone and ozonation in the presence of ZSM-5 zeolites and alumina ( $C_0$  (cum) =  $19.2 \pm 0.5$  mg/L,  $C_0$  (DCB) =  $3.5 \pm 0.2$  mg/L, and  $C_0$  (TCB) =  $0.5 \pm 0.1$  mg/L;  $T = 20^\circ\text{C}$ ; pH = 3.0, 6.2 and 13.0;  $\text{pH}_{30\text{min}} = \text{pH}_0 \pm 0.3$ ; catalyst amount = 5 g;  $V = 490$  mL;  $\text{O}_3 = 0.1$  mg/min).

case of studied VOCs which agrees with our hypothesis that VOCs ozonation on zeolites occurs via molecular ozone reactions.

### 3.2.2. pH changes during the ozonation and catalytic ozonation process

The presence of contaminants on the catalysts may change the initial pH of water and hence can affect the experimental results. It has been recently reported that alkaline contaminants present on the surface of alumina lead to higher ozone decomposition in the presence of alumina when compared with ozonation alone [11]. Therefore, it is important to monitor pH during the ozonation and catalytic ozonation process. In this study pH changes were studied in the presence of pollutants. The results presented in Fig. 3 indicate that despite small variations from initial pH no significant change in pH ( $\text{pH}_0 \pm 0.3$ ) was observed during ozonation alone and catalytic ozonation on ZSM-5 zeolites and alumina. It can be therefore concluded that observed negligible variations of pH during catalytic ozonation do not affect the overall process.

### 3.2.3. Formation of chloride ions

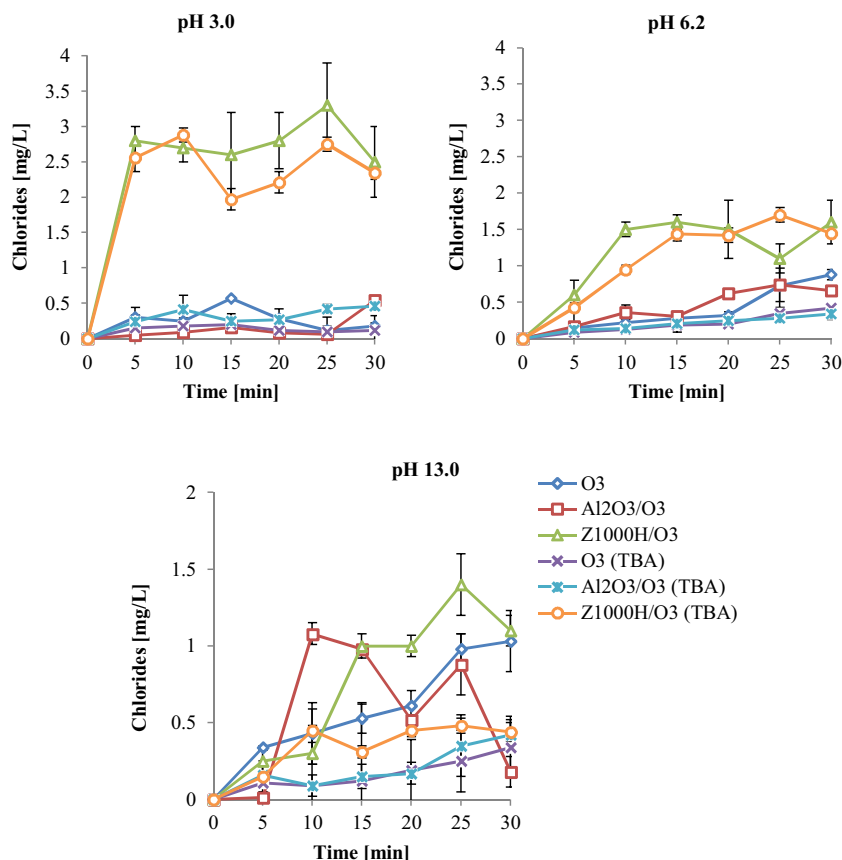
The formation of chlorides was studied during catalytic ozonation of VOCs (cumene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene) on alumina and ZSM-5 zeolites at selected pH values. The formation of chlorides during ozonation and catalytic ozonation processes may help to verify degradation of VOCs, which may further lead to better understanding of mechanisms governing both catalytic systems [30]. The results presented in Fig. 5 show that the formation of chlorides in the case of ozonation in the presence of alumina was very low when compared with zeolites. This may be due to the low adsorption of chlorinated VOCs on alumina [17]. As

previous findings indicate [17], surface reactions are considered to be important in the effective degradation of pollutants on alumina. Low formation of chlorides during ozonation on alumina might be also linked with the fact that alumina facilitates ozone decomposition but molecular ozone reactions are favoured in the case of VOCs degradation. Among the zeolites, high silica zeolites (Z1000H, Z900Na) showed significantly higher chlorides formation (Fig. 5). This clearly suggests that high silica zeolites lead to higher degradation of chlorinated VOCs when compared with their low silica equivalents (Z25H, Z25Na). From these results it can be hypothesised that adsorption of pollutants on the surface of the catalyst is a critical stage of the catalytic process [5]. The results further indicated that at pH 13.0 the chlorides formation was similar to single ozonation (Fig. 5). This may be due to the lack of catalytic activity at this pH [14]. It is also important to mention that no significant change in the pH of solution was observed in all experiments throughout 30 min reaction time.

## 3.3. Mechanisms of catalytic ozonation

### 3.3.1. Effect of tert-butyl alcohol on the VOCs removal rates

A comparative study of VOCs ozonation has been conducted on a selected zeolite (Z1000H), alumina and using ozonation alone in the presence and absence of *tert*-butyl alcohol (TBA). Pseudo first order VOC decomposition rate constants are presented in Tables 2 and 3. The results clearly indicate that VOCs removal on Z1000H/ $\text{O}_3$  remained unaffected in the presence of TBA (Tables 2 and 3). However, in the case of alumina conclusive results have not been obtained, as there was no significant removal of VOCs in the case of alumina as compared to ozonation alone (Tables 2 and 3). This



**Fig. 6.** Effect of TBA on chlorides formation during VOCs ozonation alone and ozonation in the presence of ZSM-5 zeolites and alumina ( $C_0$  (cum) =  $19.2 \pm 0.5$  mg/L,  $C_0$  (DCB) =  $3.5 \pm 0.2$  mg/L, and  $C_0$  (TCB) =  $0.5 \pm 0.1$  mg/L;  $T = 20^\circ\text{C}$ ; pH = 3.0, 6.2 and 13.0; pH<sub>30min</sub> = pH<sub>0</sub>  $\pm$  0.3; catalyst amount = 5 g; V = 490 mL; O<sub>3</sub> = 0.1 mg/min; TBA = 50 mg/L).

may be due to the lack of adsorption of VOCs on alumina's surface [17].

It is important to highlight here that the lack of catalytic activity at pH 13 for both zeolites and alumina is to be expected as at a higher pH, due to the presence of hydroxide ions, free hydroxyl radicals are more readily formed. Such observations indicating the inhibition of catalytic activity of zeolites and alumina have been reported in previous studies [6,14,17].

### 3.3.2. Effect of tert-butyl alcohol on the formation of chloride ions

In order to investigate the mechanism of catalytic ozonation in the presence of zeolites and alumina, the formation of chlorides as a result of degradation of the chlorinated compounds was investigated in the presence and absence of TBA. The results presented in Fig. 6 show that formation of chlorides as a result of ozonation of chlorinated VOCs on Z1000H was not affected to a high extent in the presence of TBA at pH 3 and 6.2. For example, the concentration of chlorides was 1.6 mg/L after 30 min when solution was ozonated on Z1000H at pH 6.2 and it was 1.5 mg/L in the presence of TBA under similar conditions. In contrast to experiments undertaken at pH 3 and 6.2, formation of chlorides was reduced in Z1000H/O<sub>3</sub> at pH 13 (Fig. 6). For example, the concentration of chlorides was about 1.1 mg/L and it was reduced to 0.44 mg/L in the presence of TBA after 30 min. Interestingly, similar decrease in the chlorides formation was observed in the presence of TBA in both catalytic and single ozonation experiments (Fig. 6). This suggests that the decrease of chlorides formation in the case of Z1000H/O<sub>3</sub> at pH 13.0 takes place, similarly to ozonation alone, due to the influence of scavenging effect of TBA on radicals produced in bulk solution. It is also important to emphasise that a significant reduction in chlorides formation was also observed at pH 6.2 in the case of Al<sub>2</sub>O<sub>3</sub>/O<sub>3</sub>

(for example the concentration of chlorides was 0.66 mg/L after 30 min without TBA and it was 0.34 mg/L in the presence of TBA at pH 6.2, Fig. 6). These results further support our hypothesis that ozonation in the presence of alumina operates through the radical mechanism while ZSM-5 zeolites facilitate degradation of VOCs through molecular ozone reactions on their surface. It is important to mention here that the above hypothesis is in agreement with recent findings [6,17].

### 3.3.3. Proposed mechanism

Previous studies on VOCs ozonation indicate that zeolites catalyse the removal of VOCs when compared with ozonation alone. In contrast, alumina does not remove VOCs [6,17]. However, it is important to mention, that some reports imply that alumina does catalyse the removal of VOCs in water [18,20]. It was reported that adsorption of pollutants on the alumina surface was found to be an important step in the catalytic process [20]. In current study the lack of catalytic activity of alumina towards VOCs (cumene, dichlorobenzene and trichlorobenzene) may be due to the lack of adsorption of studied VOCs on alumina's surface [17]. The results presented in this work provide further evidence. The significantly higher concentrations of chlorides formed in the presence of ZSM-5 zeolites when compared with ozonation alone and ozonation on alumina clearly suggest that zeolites catalyse the degradation of VOCs. Furthermore, the concentration of chlorides during VOCs ozonation on zeolites in the presence of hydroxyl radical scavengers (TBA) was found not to remain constant when compared with ozonation on zeolites without TBA. This clearly suggested that zeolites do not promote ozone decomposition leading to the formation of hydroxyl radicals. Furthermore, it was found that catalytic activity of zeolites was the highest in the case of zeolites with high

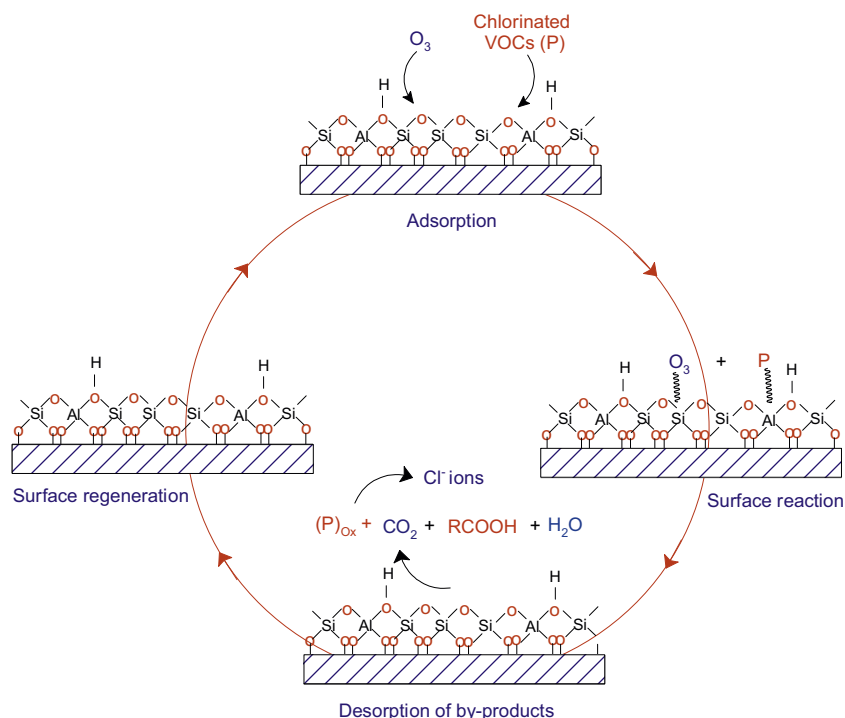


Fig. 7. Proposed mechanism of VOCs ozonation on zeolites.

silica content. This may be due to high adsorption of VOCs on the surface of zeolites followed by their reactions with molecular ozone [5,6]. The mechanism of catalytic ozonation in the presence of zeolites has been proposed (based on this and previous findings) as indicated in Fig. 7. It clearly indicates that adsorption of VOCs plays a vital role in the catalytic ozonation process.

In contrast to zeolites, ozonation on alumina does not lead to increased generation of chlorides when compared with ozonation alone at studied pH values. This may be due to the lack of adsorption of VOCs on the alumina surface. Surface reactions are considered to be important in the catalytic ozonation process. This suggests that alumina may not be an effective catalyst for the removal of studied VOCs. This is in agreement with some of the previous findings [17]. Previous reports have also indicated that alumina may decompose aqueous ozone leading to the production of active oxygen species [14,22,24]. It is further reported that surface hydroxyl groups may be the active sites [14,22,24]. However, some reports have contradicted this and suggested that aqueous ozone is not decomposed by alumina [21]. Qi et al. [23] confirmed that alumina promotes the generation of hydroxyl radicals but the group claimed that surface hydroxyl groups of alumina do not interact with ozone. Other reports further suggested that molecular ozone reactions may be involved [9,16]. The results presented in this work clearly indicate that alumina is not an effective catalyst for studied VOCs and this may be due to the lack of adsorption of VOCs on alumina's surface. The lack of generation of chlorides on alumina in comparison with zeolites further supports this hypothesis.

#### 4. Conclusions

The following are the main conclusions.

1. ZSM-5 zeolites, as opposed to alumina, are the effective catalysts of VOCs degradation during ozonation. The surface reactions were found to be important in the catalytic ozonation process

2. The ZSM-5 zeolites with high silica to alumina ratios were found to be more effective in the decomposition of VOCs when compared to low silica zeolites.
3. Catalytic ozonation on ZSM-5 zeolites proceeds via direct attack of molecular ozone on the adsorbed chlorinated pollutants leading to the generation of chlorides.
4. TBA, a hydroxyl radical scavenger, does not influence catalytic activity of zeolites.
5. The decomposition of pollutants occurs via pseudo first order kinetics.

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